

point to a similar conclusion; although no great alteration in density has been produced, yet there is a sign that a kind of separation is being effected electrically. There is also in favour of the supposition the unlikelihood that two or more gases, so like one another as the constituents of helium, should exist with densities so near each other; and the probability that some separation should have been detected by aid of the spectroscope.

Lastly, the refractivities of both gases, if there be two, appear to be equally abnormal; now, different gases have different refractivities in no known relation to their densities, as, for example, hydrogen 0.5, oxygen nearly 1. But the refractivities of the different portions of helium are proportional to their densities; a statement which is true of any one gas, inasmuch as refractivity is directly proportional to pressure, *i.e.*, mass in unit volume. The refractivity of helium, also, is so small that it totally differs in this respect, as, indeed, it does in most of its physical properties from every other gas, and it is moreover a monatomic gas. It is therefore permissible to seek for an explanation of its remarkable properties in framing any hypothesis which admits of being put to the test.

“On the Spectrum of Cyanogen as produced and modified by Spark Discharges.” By W. N. HARTLEY, F.R.S., Royal College of Science, Dublin. Received July 13, 1896.

The Production of Cyanogen in the Electric Arc.—The very careful and numerous experiments of Liveing and Dewar* have very generally been accepted as affording evidence sufficient to establish the existence of an emission spectrum of cyanogen as distinct from that of carbon in the electric arc. Kayser and Runge,† though at first disinclined to accept such a conclusion, obtained additional evidence by experimenting with the arc in air, and in carbon dioxide. They found that the ordinary carbon spectrum and that of cyanogen appeared with rapidity alternately in the arc in air, though there could be no difference in temperature sufficient to account for the production of two different carbon spectra. With the poles immersed in carbon dioxide no such changes were seen, the carbon spectrum alone being visible, which evidence led them to concur in the views of Liveing and Dewar. The chief evidence of the existence of a cyanogen spectrum rests on the fact that this substance is actually synthesised in the arc when nitrogen is present, and because without

* ‘Roy. Soc. Proc.’ vol. 30, pp. 152—162, 494—509: vol. 34, pp. 123—130 and pp. 418—429.

† “Ueber die Spectren der Elemente. Zweiter Abschnitt. Ueber die im galvanischen Lichtbogen auftretenden Bandenspectren der Kohle.” ‘Abh. K. Preuss. Ak. Wiss.’ 1889, p. 9.

nitrogen, elementary carbon does not yield the same spectrum, no matter what the temperature may be; and lastly, that cyanogen gas burns with a flame of which the banded spectrum is known as that of cyanogen by reason of the foregoing facts. Furthermore, I have found by recent experiments that when a condensed spark is passed between electrodes of gold in an atmosphere of cyanogen, the same spectrum is photographed.

If we admit that under conditions favourable to synthesis from its elements, cyanogen is capable of emitting a spectrum of its own, this emission should occur only at the moment of its formation, but while giving consideration to this view we are met by the difficulty that the flame of cyanogen burning in oxygen would less probably emit a spectrum of the compound substance itself, which is being burnt, than a spectrum of the products of its combustion, or of the separated elements of which it is composed, which are nitrogen and carbon; and for this reason, that the process it is passing through is not a synthetical but an analytical one. Indeed it has been shown by Liveing and Dewar* that when cyanogen is exploded with oxygen it gives a bright continuous spectrum, but no cyanogen spectrum, or carbon bands, or carbon lines.

I shall have to refer to these facts and adduce later evidence of the existence of the cyanogen spectrum in the latter part of this paper.

Evidence derived from their Spectra, of the progress of Chemical Changes in Flames.—In support of the view that the flame of burning cyanogen ought to exhibit the spectrum of carbon, I may mention the following facts which have been recorded during a very careful examination of a number of photographs of the spectra of flames which were obtained by burning gases under normal atmospheric conditions.

The majority of these photographs were taken in 1882.

<i>The Combustion of Compound Substances.</i>	<i>Components of the Spectra photographed.</i>
Hydrocarbons in oxygen.	Carbon bands, cyanogen bands, water-vapour lines.†
Sulphuretted hydrogen in air and in oxygen.	Sulphur bands and water-vapour lines.
Ammonia in air.	Water-vapour lines.
Carbon disulphide in air.	Sulphur bands only.
Carbon disulphide and nitric oxide.	Sulphur bands only.
Carbon monoxide and oxygen.	Continuous spectrum of carbon monoxide. Faint lines due to carbon, very few in number.

* 'Roy. Soc. Proc.,' vol. 49, p. 222. "On the Influence of Pressure on Flames."

† When nitrogen is present, Liveing and Dewar have observed the formation of NO_2 (*loc. cit.*).

By the combustion of ammonia in oxygen, water vapour lines are produced, and new bands and groups of lines attributed by Eder and Valenta to ammonia. Some of these are, however, due to a compound other than ammonia.

It will be observed that compounds during combustion as a rule show the spectra of one or other of their constituents, or of both. In the case of hydrogen compounds they show the product of the combustion of hydrogen, which is a substance of great stability, and can therefore exist at a high temperature.

In the nitric oxide and carbon disulphide spectrum, the sulphur bands, which are very strong, probably obscure those of carbon. There is a strong continuous band of rays which would likewise serve to obscure them.

C. Bohn* has examined the spectra seen in a Bunsen burner of the form devised by Teclu† (which is simply a modification of that described by Smithells), and compared the spectra with that obtained by Swan, and with the discharge in Geissler tubes containing various hydrocarbon gases. He concludes that it is impossible to define a carbon band spectrum, as the differences observed were greater than could be accounted for by alterations in temperature and pressure. He also states that sulphur, hydrogen, and carbon disulphide, also carbon monoxide, were burnt, but that all these flames yielded continuous spectra. This statement is incorrect, or at least inaccurate.‡ Bohn's observations were evidently made on too limited a region of the spectrum, and without the aid of photography. On Bohn's paper Eder has made some observations, quoting both his measurements in the visible and ultra-violet spectrum, which he observes must have been unknown to Bohn.§

He describes in what manner and by what causes the edges of the carbon bands are altered in position or in character.

The observations of Eder on the spectra of hydrocarbon flames are quite in agreement with those previously communicated by me to the Royal Society on the oxyhydrogen flame spectrum and the oxy-coal gas spectrum.

On certain Chemical Changes occurring in the Spark and in Flames.

Though it is now accepted as a fact that the arc in air yields the spectrum of cyanogen, and that the evidence of this is, first, the identity of certain bands observed in the flame of burning cyanogen

* 'Zeitschrift für physikal. Chemie,' vol. 18, p. 219, 1895.

† 'J. prak. Chemie' [2], vol. 52, pp. 145—160, 1895.

‡ "Flame Spectra at High Temperatures" ('Phil. Trans.,' A, vol. 185, pp. 161—212, 1894).

§ "Ueber Flammen und leuchtende Gase" ('Zeitschrift für physikal. Chemie,' vol. 19, p. 1, 1896).

with those seen in the arc; second, that these bands cannot be due to the effect of an alteration in temperature, giving rise to a second spectrum of carbon; nevertheless, as I have elsewhere pointed out,* cyanides in a condensed spark do not produce this spectrum, no matter whether they are extremely stable cyanides, such as that of potassium, or those of the most easily decomposable character, such as mercuric cyanide. This appeared to me to mark the inadequacy of the facts derived solely from observations on the arc, to establish the existence of a definite cyanogen spectrum. Moreover, it was shown that lines somewhat resembling the edges of cyanogen bands are seen when graphite poles are moistened with water and the spark is passed through air; these lines are intensified and developed into bands when the water contains ammonium chloride, calcium chloride, or zinc chloride, and the bands become stronger as the solution used is more concentrated.

If the lines observed are the edges of bands belonging to the cyanogen spectrum, by what means do the chlorides give rise to their production? No one has yet supplied the answer to this question, neither has it been proved that these lines in the spectrum of graphite are the edges of cyanogen bands, though Eder† and Valenta state that they are such because the wave-length measurements are approximately the same.

I believe that I am now able to offer an explanation of the action of the concentrated solutions of chlorides, and to prove in addition, that the bands and lines are really due to cyanogen and not to elementary carbon.

If hydrochloric or any other mineral acid be carefully tested, it is found to contain ammonia. The only ammonia-free acid is sulphurous acid freshly prepared by passing sulphur dioxide gas into water, carefully freed from ammonia and from any possible contamination with it. If from the usual samples of so-called pure mineral acids, salts of calcium or zinc be prepared, the ammonia salt present is not eliminated, but it goes into solution and crystallises out with such calcium or zinc compound, or, if the salt does not crystallise, it remains in solution, and, as a consequence, the salt will show in its solution the effect of a larger proportion of ammonium salt, according to its degree of concentration. Hence if the bands, said to be cyanogen bands, are due to the nitrogen of the ammonia present, the spectrum of the graphite poles will exhibit the bands more strongly, as there is less water in the solution. But this does not account for

* 'Phil. Trans.,' vol. 175, p. 49, Part I, 1884, and 'Roy. Soc. Proc.,' vol. 55, p. 344, "On Variations observed in the Spectra of Carbon Electrodes, and on the Influence of one Substance on the Spectrum of another."

† 'Wien, Akad. Wiss. Denkschriften,' vol. 60, 1893, "Line Spectrum of Elementary Carbon."

the fact that the spark does not show the cyanogen bands when cyanides are submitted to its action. In this case it is possible that the temperature is too high, and that the cyanogen is decomposed, possibly by oxidation, for there can be no doubt that such condensed sparks are at a higher temperature than that of the arc. We know, too, that several metals are oxidised when volatilised in the spark, if not entirely at least partially.* But by using gold electrodes with the cyanides we do not obtain even a carbon spectrum.

Here again, possibly, the carbon is oxidised, and we know that carbon dioxide in carbonates yields no spectrum of carbon, nor any lines peculiar to carbon dioxide.

I have sought in every direction for a reasonable explanation of that which, up to the present, has proved inexplicable, in order that by working on some hypothesis one might devise a means of putting the matter to experimental proof. This has now been accomplished in the following manner.

An almost saturated solution of pure crystallised potassium cyanide was put into a tube fitted with graphite electrodes in the manner described in a previous communication.†

The apparatus was fitted into a horizontal wooden tube with a window of quartz at one end, and carbon dioxide was passed into the tube until filled. The spark was then passed for five minutes, and again for ten minutes, a photograph being taken of the two spectra. The instrument used gave a dispersion equal to four quartz prisms. A glass tube with a similar window of quartz was fitted with gold electrodes and filled with cyanogen gas, and another spectrum was photographed. A fourth spectrum was then obtained by passing cyanogen into the wooden tube containing the graphite electrodes; after the carbon dioxide had been expelled by air and replaced by cyanogen, the U-tube was filled up with the solution of potassium cyanide. In all four cases the principal group of the cyanogen bands was obtained, but it was not very strong. A flame of cyanogen was then photographed with exposures varying from one to two, five, and ten minutes. A beautiful series of spectra was obtained, and the lines belonging to the edges of bands constituting the principal group were found to coincide exactly with those photographed from the potassium cyanide solution when the spark was passed in an atmosphere of carbon dioxide and in cyanogen, also when the spark was passed between gold electrodes in cyanogen. These appear to be the bands referred to by Eder and Valenta, which were described as *carbon bands*‡ when graphite electrodes were used with the spark

* 'Roy. Soc. Proc.,' vol. 49, p. 448, "On the Physical Characters of the Lines in the Spark Spectra of the Elements."

† 'Phil. Trans.,' vol. 175, p. 49, 1884.

‡ Hartley and Adeny, 'Phil. Trans.,' vol. 175, p. 63, Part I, 1884.

in air. From the modification of their appearance, and the measurements originally made from them, their identity was not quite apparent, although probable.

It thus appears that, with the spark, the cyanogen spectrum is nothing like so strongly marked, as is the case with the flame of the gas, only one group of bands being represented, and that when the spectrum is taken in air the cyanogen does not appear, because in all probability the substance is oxidised.

I have already stated that the formation of cyanogen which yields the characteristic spectrum is a synthetical operation, that compound substances, when burnt in flames, do not, as a rule, emit the spectrum of the compound, but the spectrum of one or more of the elements of which it is composed, or that of one or other of its products of combustion.

How then are we to account for the cyanogen spectrum in the flame of burning cyanogen?

The conditions under which combustion takes place are these: there is an excess of the gas, the temperature of the flame is exceedingly high, and the gas within it is not in contact with a solid substance, hence immediate decomposition does not occur, and the gaseous compound is heated to incandescence.

“Variation in *Portunus depurator*.” By ERNEST WARREN, B.Sc.,
Demonstrator of Zoology at University College, London.
Communicated by W. F. R. WELDON, F.R.S. Received
July 1, 1896.

The following measurements were undertaken at the proposal of Professor W. F. R. Weldon, and to him I am greatly indebted for many suggestions, and for the kindly help he has always so readily given me.

The crabs were obtained from the Biological Station at Plymouth, and sent at intervals during a period of about two years, dating from the autumn of 1893. Only males were measured. Seven measurements were made on each individual, corresponding to those made by Professor Weldon on the female of *Carcinus moenas* (‘Roy. Soc. Proc.,’ vol. 54).

1. Carapace length, AB (fig. 1).
2. Total carapace breadth, CC’.
3. Frontal breadth, DD’.
4. Right antero-lateral, AC.
5. Left antero-lateral, AC’.
6. Right dentary margin, CD.
7. Left dentary margin, C’D’.